

SECTION 16

FIELD MEASURABLE PHYSICAL/CHEMICAL CHARACTERISTICS

PERFORMANCE OBJECTIVES:

To measure physical/chemical characteristics of a sample that are representative of field conditions as they exist at the time of sample collection

- By selecting the appropriate meter/instrument(s)
- By properly calibrating each instrument(s)

16.1 Introduction

Temperature, specific conductance (conductivity), hydrogen-ion concentration (pH), turbidity, dissolved oxygen (DO), chlorine, salinity, flash point, and halogen test will be the parameters discussed in this section. The order in which the measurements are made is very important. The sections will be discussed in the most applicable order. References for each section can be found at the end of the section listed in order with respect to the meter discussed.

Numerous meters/instruments are commercially available. Some meters are capable of numerous measurements which may include: pH, temperature, conductivity, DO, salinity, and turbidity; therefore, individual meters discussed here are not necessarily the only ones available. However, the setup and use of all instruments should follow a basic format to imply a consistency of use.

Regardless of the brand of meter used, all meters should be properly maintained and operated in accordance with the manufacturer's instructions and the calibration should be checked prior use.

16.2 Temperature

Temperature is a measure of hotness or coldness on a defined scale.

Three types of thermometers are available:

- Digital (thermo-couple) thermistor
- Glass bulb mercury filled
- Bi-metal strip/dial indicator

Calibration:

Whichever type of thermometer is used, it should be calibrated semi-annually against a National Instrumentation Standards and Technology (NIST) certified thermometer.

Note: Thermistors should be checked against a mercury bulb thermometer prior to use and should agree within ± 0.5 °C.

Inspection:

All thermometers should be inspected for leaks, cracks, and/or function prior to use.

Note: A broken glass bulb-mercury filled thermometer can contaminate samples by the release of mercury vapors.

Procedures: (Make measurements in-situ when possible)

1. Clean the probe end with de-ionized water and immerse into sample.
2. Swirl the thermometer in the sample.
3. Allow the thermometer to equilibrate with the sample.
4. Suspend the thermometer away from the sides and bottom to observe the reading.
5. Record the reading in the log book. Report temperatures readings to the nearest 0.5 °C.

Note: Always clean the thermometer prior to storage and/or use.

Units:

Degrees Celsius (°C) or Degrees Fahrenheit (°F)

Conversion Formulas:

$$^{\circ}\text{F} = (9/5 \text{ } ^{\circ}\text{C}) + 32 \quad \text{or} \quad ^{\circ}\text{C} = 5/9 (^{\circ}\text{F} - 32)$$

16.3 Specific Conductance (Conductivity)

Conductivity is defined as the quality or power of conducting or transmitting.

Meter(s) available:

- Wheatstone bridge meters are typically used for measuring conductivity.

Calibration:

The meter should be calibrated in accordance with the manufacturer's instructions. A two-point standard should be used to insure the accuracy of the meter. Conductivity may be affected by temperature; therefore, temperature should be read first so that appropriate adjustments can be made in accordance to the manufactures instructions.

1. Check and record the temperature of the standard solutions.
2. Rinse the probe with analyte-free water before immersing it in the standards solution.
3. Immerse the probe in the first standard solution and record the results.

Note: Make sure the meter is "ON".

4. Rinse the probe and immerse it into the second standard solution and record results.

Note: If the meter is not accurate to within $\pm 10\%$ of the standards, correct the problem before proceeding.

Procedures:

1. Collect the sample and check and record its temperature.
2. Correct the instruments temperature adjustment to the temperature of the sample (if required).
3. Immerse the probe in the sample keeping it away from the sides and bottom of the container. It is important that the enter portion of the probe be wetted by the sample. This will be evident when some of the sample water is seen coming out of the small weep hole.
4. Record the results in a log book.
5. Rinse probe.

Units:

Conductivity units are measured in micromhos per centimeter ($\mu\text{mohs/cm}$) at 25°C . Results should be reported to the nearest ten (10) units for readings below $1,000 \mu\text{mohs/cm}$ @ 25°C and to the nearest one hundred (100) units for reading above $1,000 \mu\text{mohs/cm}$ @ 25°C .

16.4 Hydrogen Ion Concentration (pH)

The pH is defined as the negative logarithm of the effective hydrogen-ion concentration or hydrogen-ion activity in grams equivalents per liter used in expressing both acidity and alkalinity on a scale which ranges from 0 to 14 with 7 representing neutrality.

Meter(s) available:

- Orion Model 399A
- Orion SA 250 or 230A
- Hydrolab Surveyor II
- YSI 3530, 3500 Water Quality Monitoring System

Calibration: (Follow manufacturer's instructions with the following as a minimum)

Note: The pH of the sample to be tested should be estimated either from historical data or by using a four-color pH indicator paper or equivalent. Using this information, the two buffering points for calibration can be determined.

1. Remove the meter from storage and allow it to equilibrate to ambient temperature.
2. Use a thermometer and determine the temperature of the buffering solutions and record.
3. Select either pH 4 and pH 7 or pH 7 and pH 10 solutions as described above.
4. Rinse the probe with analyte-free water and immerse it into the first buffer (pH 7) and record.
5. Rinse the probe with analyte-free water and immerse it into the second buffer and record.
6. Rinse and store the probe in a container filled with analyte-free water.

Procedures:

1. Collect a sample. Measure the temperature prior to measuring the pH.

Note: If the temperature of the sample differs by more than 2°C or approximately 4°F, refer to the manufactures instructions on how to adjust for temperature variations.

Note: When the pH meter response is slow, unstable, or non-reproducible, it may be necessary to check the conductivity. If the conductivity is lower than 20 to 30 $\mu\text{mhos/cm}$ then add 1 ml of 1M potassium chloride solution per 100 mls of sample. Recheck the pH and record.

2. Immerse the probe in the sample keeping it away from the sides and bottom of the sample container. Allow ample time for the probe to equilibrate with the sample.
3. While suspending the probe away from the sides and bottom of the sample container, record the pH.
4. Rinse the probe with analyte-free water and store it in a analyte-free water filled container until the next sample is ready.

Operational check:

1. While in use, periodically check the pH by rinsing the probe with analyte-free water and immersing it into the pH 7 buffer solution.
2. Perform a post calibration at the end of the day and record all findings.

Units:

Units of pH are Standard Units (SU) and should be read in one-hundredths (0.01) and recorded in tenths (0.1).

Note: If the pH measurements are to be used for RCRA regulatory purposes and when the pH approaches the alkaline end ($\text{pH} \geq 11.0$) of the scale, the pH measurements should be made by a qualified analyst using laboratory quality equipment to control the sample at $25^{\circ}\text{C} \pm 1^{\circ}\text{C}$.

16.5 Turbidity

A nephelometer/turbidimeter is used in comparing the turbidity of liquids by viewing light through them and determining how much light is eliminated.

Meter(s) available:

- Hach 2100P Turbidimeter

Calibration:

1. Turn the meter "ON".
2. Rinse the sample cell 3 times with organic free or deionized water.
3. Fill the cell to the fill line with organic free or deionized water and then cap the cell.
4. Use a non-abrasive lint-free paper or cloth (preferably lens paper) to wipe off excess water and streaks.
5. Open the cover and insert the cell (arrow to the front) into the unit and close the cover.
6. Press "READ" and wait for the 'light bulb' icon to go off. Record the reading.
7. Using the Gelex standards, repeat steps 4, 5, and 6. Record all findings (note anomalies).

Procedures:

1. Collect a specific sample or use a portion of the sample that is collected for pH, temperature, or conductivity analysis, and pour off enough to fill the cell to the fill line (approximately $\frac{3}{4}$ full) and replace the cap on the cell.
2. Wipe off excess water and any streaks with non-abrasive lint-free paper or cloth (lens paper).
3. Place the cell in chamber of the 2100P with the arrow towards the front and close the cover.
4. Press "READ" and wait for the 'light bulb' icon to go off. Record the reading.
5. Rinse the cell with organic-free or analyte-free water.
6. For the next sample, repeat Steps 1-5.

Operational check:

1. Periodically check the turbidity meter by using the standards provided.
2. Perform a post calibration at the end of the day and record all findings.

Units:

Turbidity measurements are reported in nephelometric turbidity units (NTUs).

16.6 Salinity

Salinity is the measure of salts of the alkali metals or of magnesium found in water. This measurement is based on the direct proportionality between the magnitude of an induced electric current and the electrical conductivity of the water in which it is induced.

Meters available:

- Beckman Model RS5-3 Portable Salinometer
- Hydrolab Surveyor II
- Scout
- Datasone Salinometer

Calibration/Maintenance:

- Follow the manufactures instructions.
- Routinely check the Beckman meter against a resistor matched to the meter.

Procedures:

- The Beckman has an accuracy of ± 0.3 parts per thousand (ppt) salinity, ± 0.05 °C temperature, and ± 0.5 millimhos/cm specific conductance.
- The Hydrolab Surveyor II, Scout, and Datasone Salinometer have an accuracy of ± 0.7 ppt at 1% full scale conductance at ± 0.1 °C.
- These meters are suited for use in brackish to saline waters having a salinity range of 0 to 40 ppt.

Units:

Units are reported as salinity in the nearest tenth of a ppt (0.1 ppt).

16.7 Dissolved Oxygen (DO)

Meter available:

- Membrane/electrode (ME) DO meter

The most common ME meters for determining the DO in water are dependent upon electrochemical reactions. Under steady-state conditions, the current or potential can be correlated with DO concentrations. Interfacial dynamics at the ME/sample interface are a factor in probe response and a significant degree of interfacial turbulence is necessary. For precision performance, turbulence should be constant.

Inspection:

- Prior to field use, the membrane of the DO meter should be inspected for air bubbles and/or holes. If air bubbles or holes exist, replace the membrane.
- The membrane should be checked for dryness. If the membrane is dry, replace and soak it in analyte-free or analyte-free water prior to calibration of the meter.

Calibration:

- Air calibrate according to the manufacturer's instructions, either in air saturated water or in a water saturated air environment.
- The ME meter can be checked and/or calibrated against the Winkler method if desired.

Procedures:

1. When making measurements, be sure that the ME stirring apparatus is working.
2. Adjust the temperature and salinity compensators (if equipped).
3. Read the dial to the nearest 0.1 mg/l and record the measurement.

To Collect a Sample:

1. When possible, measure the DO in-situ with a field probe; otherwise,
2. Collect the sample in a 300-ml BOD bottle and measure the DO with a laboratory type probe.

Note: Special care should be exercised to avoid entrainment of atmospheric oxygen or loss of DO. The sample should be collected with a DO Dunker (APHA-type) for depths less than five feet below water surface (BWS). A Kemmerer type sampler is recommended for depths greater than five feet BWS.

3. If an APHA-type DO Dunker is not available and a shallow depth sample is needed, a bucket may be used to collect a sample of water. A siphon tube should be coiled into the bucket such that the fill end is nearest the bottom. Using a 300-ml BOD bottle, allow the siphoning sample to fill and overflow the bottle for a minimum of three volumes.

4. If a Kemmerer sampler is used, the BOD sample bottle should be filled to overflowing by inserting the outlet tube of the sampler to the bottom of the bottle. The tube should be withdrawn slowly as the bottle is allowed to overflow three times its volume. Care must be exercised to prevent turbulence or the formation of bubbles when filling the bottle.

Duplicate analyses should agree within ± 0.1 mg/l.

Units:

Units should be reported in mg/l.

Limitations:

- Dissolved inorganic salts are a factor with the performance of DO probes.

Note: The presence of inorganic salts must be determined.

- Reactive gases which pass through the ME probes may interfere with the DO analysis. For example, chlorine will depolarize the cathode and cause a high probe output. Long-term exposures to chlorine will coat the anode with the chloride of the anode metal and eventually desensitize the probe. Hydrogen sulfide will interfere with the ME probes if the applied potential is greater than the half-wave potential of the sulfide ion.
- Dissolved oxygen ME probes are temperature sensitive, and temperature compensation is normally provided by the manufacturer (see manufacturers instructions).

16.8 Total Residual Chlorine

Meter(s) available:

- Pocket colorimeter
- Hach DR-100 Colorimetric (DPD) kit -- n,n-diethyl-p-phenylenediamine (DPD) may be used for natural waters or waters treated with chlorine.

Note: The Hach reagents and colorimeter or spectrophotometer are accepted by the US-EPA for NPDES monitoring if used in accordance with approved procedures. The pre-printed calibration scales provided by the manufacturer are based on factors developed under ideal conditions and are only acceptable if verified. The calibration scale must be initially verified using multiple standards and a blank. The calibration scale or curve must be verified at least daily using a blank and one **high** and one **low** standard representative of the linear working range. These standard checks must agree within $\pm 10\%$ of the original scale or a new curve must be prepared. Verification data should be recorded and maintained on file (See Standard Methods).

Use either 1-cm or 2.5-cm cells.

Inspection:

- Each meter should be visually inspected before and after each use. Report any discrepancies to the FEC.
- Check the battery strength.
- Insure that the reagents are fresh before field trips.

Calibration:

- The calibration scales must be calibrated onsite with a minimum of three points: a blank and two known standards that bracket the expected sample concentrations.

Note: If the DPD kit is used, the method must adhere to the requirements set forth in Standard Methods.

Reagents/Standards:

- DPD total chlorine powder packets.

Note: The packets deteriorate in the presence of moisture. The packets should be discarded if they have caked or have turned brown.

The DPD oxalate is very toxic. DO NOT handle with unprotected hands or ingest. If accidentally spilled on skin or ingested, seek medical attention immediately.

- Chlorine demand-free water (See Standard Methods, Method 4500 Cl for directions in preparing the ASTM Standard D1193 "Consumption of Potassium Permanganate").

- Potassium permanganate stock -- Prepare a stock solution containing 891 mgs/1000 mls.
- Potassium permanganate working stock 10 ppm -- Prepare working stock solution containing 10 mg/l KMnO_4 by diluting 10 mls of D.8.5.4 stock solution to 1 liter.

Note: The stock should be stable for approximately 5 days if kept cool and away from light.

- Potassium permanganate calibration standards -- Prepare calibration standards from the working stock solution and/or KMnO_4 calibration standard solutions for each day of use.

Note: KMnO_4 standards will fade rapidly (within 15 minutes) if chlorine demand-free water is not used.

Calibration Standard (mg/l)	mls of Working Stock/100 mls
0.05	10.0 of 0.5 mg/l std.
0.10	10.0 of 1.0 mg/l
0.5	5.0 of 10 mg/l
1.0	10.0 of 10 mg/l
2.0	20.0 of 10 mg/l

Procedures: for total chlorine concentrations ranging between 0 - 2 $\mu\text{g/l}$

1. Fill a clean 2.5-cm cell to the 10-ml mark with a sample.

Note: The sample should have a pH between 6 and 7 SU. If necessary, adjust with 1N sulfuric acid or 1N sodium hydroxide.

2. Open a DPD total chlorine powder packet and add the contents to the sample cell.
3. Replace the cap on the cell and swirl to mix.

Note: It is not necessary for all of the particles to dissolve to obtain an accurate reading. The pH of the sample containing the DPD buffer packet must be between 6.2 and 6.5 SU.

4. Allow at least 3 minutes but not more than 6 minutes before moving to the next step (see and follow manufactures instructions for reaction times).
5. Open the light shield, turn the right set knob fully clockwise, and place the 1-cm cell in the left set position of the sample well holder. Press the cell down firmly to seat it in the holder.
6. Hold the button down. While doing this, adjust the left set knob to align the meter needle with the arrow at the extreme left of the scale.

7. Remove the cell from the holder.
8. Fill a clean 2.5-cm sample cell with the sample. Cap the cell and place it into the cell holder. Press it firmly to seat and close the light shield.
9. Set the colorimeter by holding the "ON" button down while adjusting the right set knob to zero. Open the light shield and remove the sample cell.
10. Fill a clean 1-cm sample cell with the solution from step 2, cap the cell, and place into the cell holder.
11. Press the "ON" button down and hold it until the meter stabilizes.
12. Read and record the mg/l of total chlorine from the upper (2.5-cm) scale.

Procedures: for total chlorine concentrations ranging between 0 - 3.5 mg/l

- 1 - 6. Same steps as previously listed.
7. Rotate the cell to the right position.
8. Fill a clean 1-cm sample cell with the sample, cap the cell, and place it into the cell holder.
9. Set the colorimeter by holding the "ON" button down while adjusting the right set knob to zero. Open the light shield and remove the sample cell.
10. Fill a clean 1-cm sample cell with the solution from step 2, cap the cell, and place it into the cell holder.
11. Press the "ON" button down and hold it until the meter stabilizes.
12. Read and record the mg/l of total chlorine from the upper (1-cm) scale.

Verification:

- Duplicate chlorine residual analyses should agree within ± 0.01 mg/l.

Units:

- mg/l total chlorine

Limitations:

- Do not use with or in the presence of any oxidizing agents, e.g., oxidized manganese interferes with the DPD reagent ($1 \mu\text{g/l MnO}_4 \sim \mu\text{g/l Cl}_2$).

16.9 Flash Point

The following test method is to determine if a volatile material's flash point is within established limits.

Apparatus:

- ERDCO Rapid Tester Model RT-1, Flash Point Analyzer

Calibration:

- The repeatability and reproducibility for this instrument are in accordance with the respective standards:

• p-xylene	78.0 ± 1.0°F
• n-butanol	97.9 ± 1.7°F
• n-undecane	145.4 ± 2.0°F
• n-hexadecane	270.5 ± 2.0°F

Operational Procedures:

1. Plug in the ERDCO and turn it on.
2. Switch the rocker switch adjacent to the display to Fahrenheit or Celsius display.
3. Press the red temperature preset rocker switch and rotate the red temperature preset knob until the desired temperature appears in the display window (140°F for determining ignitability characteristics). Release the rocker switch and the actual instrument temperature will appear in the display window. The RED light next to the knob should come on indicating the heater is "ON".

Note: The preset knob for test temperature may have to be reset as the test temperature is approached.

4. If a glass bulb thermometer is used, coat the bulb with a heat transfer compound and insert it into the well in the left side of the test oven. Carefully secure the top of the thermometer in the channel.
5. Open the control valve on the butane cylinder approximately 5 turns and install. Close the control valve and place the cylinder into the instrument's receptacle. Hook the hose to the valve.
6. Open the control valve approximately one turn and light the pilot light located over the square hole in shutter lid. Adjust the pilot light for the minimum flame that will light test the jet. Adjust the test jet for the flame to 4 mm width using the pinch valve knob.

Note: Immediately above the shutter is a 4 mm referenced milled lid.

7. Make sure that the shutter lid is latched (Closed). Inject 2 cc of the sample into the port between the shutter and the latch handle. Press the 1-minute timer rocker switch until the light goes on, then return the switch to center.
8. When the timer sounds, slide the shutter back slowly (taking about 2 seconds to do this). The material under test will either flash or not flash.

Note: If a halo develops around the flame, this does not constitute a flash.

9. Lift the lid. Clean out any material which was being tested with Chem-wipes. Also clean the injection port with a pipe cleaner.

Shut Down Procedures:

1. Close the control valve on the butane cylinder.
2. Disconnect the hose.
3. Open the control valve on the butane cylinder approximately 5 turns.
4. Turn the instrument off.
5. IMPORTANT - Clean the instrument (See step 9 above). Allow ample time for the instrument to cool down before storing.

16.10 Halogen Test

This method is used to qualitatively screen wastes for the presence of halogenated compounds.

Test using copper wire and flame:

Equipment:

- Propane fuel cylinder with a torch
- Igniter source (matches, flint/bar striker, etc.)
- Stainless steel rod approximately 1 foot long and **C** to ½ inch in diameter

Note: The smaller diameter rods cool down more quickly.

- Thermally resistant handle or thermally resistant gloves
- 16 or 18 gauge copper wire
- Wire cutters

Procedure:

1. Wrap approximately 4 feet of copper wire around the tip of the rod.
2. Clean the wire and rod tip using the flame of the propane torch.

Note: When a blue flame with small yellow-orange streaks appears, the wire and rod are clean. Allow the copper wire to become "red" hot during the cleaning process (this takes from ½ to 1 minute).

3. Allow the rod and wire to cool for a minimum of 15 minutes.

Note: The wire and rod can be immersed in water to speed up the cool down time. This will not bias the results. Allow the water to evaporate completely and the rod tip should be cool to the touch before using it in the test.

CAUTION!

DO NOT IMMERSE A HOT ROD INTO A POTENTIALLY FLAMMABLE MATERIAL

4. Immerse the cooled wire and rod tip into the test material for approximately 10 seconds.
5. Remove the wetted wire/tip from the test material and allow the excess material to drip back into the container.

Note: Highly viscous material which sticks to the tip may produce a large flame.

6. Place wetted wire into the flame and observe the color produced.

Note: A bright green flame indicates the presence of halogenated material.

16.11 References

Temperature

1. Standard Methods for the Examination of Water and Wastewater, 18th Edition p. 2-59, Method 2550 B (1992).
2. Methods for Chemical Analyses of Water and Wastes, US-EPA, 170.1 (1983).

Specific Conductance (Conductivity)

3. Standard Methods for the Examination of Water and Wastewater, 18th Edition, p. 2-43, Method 2510B (1992).
4. Annual Book of ASTM Standards, Vol. 11.1, "Water," Standard D1125-91A, P. 202.
5. Methods for Chemical Analysis of Water and Wastes, US-EPA, 120.1 (1983).
6. Instruction Manual, SoluBridge® RB-5/RB-6, Beckman Instruments, Inc., Rev. January 1982.
7. Surveyor II Operating Manual, Hydrolab Corporation, Rev. A February 1985.
8. YSI Model 3560 Water Quality Monitoring System Instructions, July, 1988.

Hydrogen Ion Concentration (pH)

9. Standard Methods for the Examination of Wastewater, 16th Edition, p. 429, Method 423 (1985).
10. Instruction Manual for Models 399 A/F, 399 A/L Analog pH Meter, and SA 250 and 230A, Orion Research Incorporated.
11. Instruction Manual for Surveyor II, Hydrolab Corporation.
12. Instruction Manual for YSI Water Quality Monitoring System for the Model 3530 pH Electrode Assembly.
13. Annual Book of ASTM Standards, Part 31, "Water", Standard D1293-78(B).
14. Methods for Chemical Analysis of Water and Wastes, US-EPA, 150.1 (1983).
15. Procedure No. 501, pH Measurement in Low Ionic Strength Solutions, Orion Application Information, Orion Research Incorporated.
16. Federal Register, Vol. 60, No. 64, Tuesday, April 4, 1995 -- Rules and Regulations, 17001-17003.

Turbidity

17. Operating procedures for the Hach 2100P Turbidimeter

Dissolved Oxygen

18. Standard Methods for the Examination of Water and Wastewater, 18th Edition, p. 4-100, Method 4500-0C (1992).
19. Annual Book of ASTM Standards; Part 31, "Water," Standard D888-92(A).
20. Methods for Chemical Analysis of Water and Wastes, US-EPA, 360.1 (1983).
21. Methods for Chemical Analysis of Water and Wastes, US-EPA, 360.2 (1983).
22. Instruction Manual YSI Model 57, Dissolved Oxygen Meter, Science Division, Yellow Springs Instrument Company.

Chlorine - (DPT Colorimetric)

23. Annual Book of ASTM Standards, "Water," Standard D 1253-86(92).
24. Methods for Chemical Analysis of Water and Wastes, US-EPA, 330.1 (1983)
25. Methods for Chemical Analysis of Water and Wastes, US-EPA, 330.5 (1983).
26. Standard Methods for the Examination of Water and Wastewater, 18th Edition, Method 4500-CL D (1992).
27. Standard Methods for the Examination of Water and Wastewater, 18th Edition, p. 4-100, Method 4500- CL G (1992).
28. Instruction Manual, DR 100 Colorimeter, Model 41100-02, DPD Method for Chlorine, Hach Company, June 1983.

Salinity

29. Standard Methods for the Examination of Water and Wastewater, 18th Edition, p. 2-47 Method 2520 B (1992).
30. Instruction Manual, RS5-3 Portable Salinometer, Beckman Instruments, Inc., Revised March 1973.

Flash Point

31. Rapid Tester Model RT-1 Technical Manual, Operations and Service, November 1, 1989.